REMARKS

Favorable consideration of this Application as presently amended and in light of the following discussion is respectfully requested. The applicant has rewritten the claims into proper U.S. form.

Claims 1-34 are now in the application. Claim 1 is the only independent claim. The applicant authorizes the PTO to charge the $700.00 for the extra 14 claims over twenty. Applicant believes no additional fee is due with this request. However, if a fee is due, please charge our Deposit Account No. 03-2775, under Order No. 12834-00021-US from which the undersigned is authorized to draw.

Respectfully submitted,

CONNOLLY, BOVE,
LODGE & HUTZ, L.L.P.

Ashley I. Pezzner
Registration No. 35,646
Attorney of Record

CUSTOMER NUMBER
23416
Phone: 302-658-9141
Fax: 302-255-4270

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Atty. Docket No. 12834-00021-US

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

RE:	Application Serial No.:	10/589,844
	Applicants:	Thomas SCHMIDT et al.
	Filing Date:	August 18, 2006
	For:	HIGH-PERFORMANCE MEMBRANE ELECTRODE UNIT AND THE USE THEREOF IN FUEL CELLS
	Group Art Unit:	Unassigned
	Examiner:	Unassigned

COMMISSIONER FOR PATENTS
ALEXANDRIA, VIRGINIA 22313

SIR:

Attached hereto for filing are the following papers:

- **English Translation of WO 2005/081351**
- **Preliminary Amendment**

Applicants believe no fee is due with this request. However, if a fee is due, please charge our Deposit Account No. 03-2775, under Order No. 12834-00021-US from which the undersigned is authorized to draw. A duplicate copy of this paper is enclosed.

Respectfully submitted,
CONNOLLY, BOVE,
LODGE & HUTZ, L.L.P.

CUSTOMER NUMBER
23416
Phone: 302-658-9141
Fax: 302-255-4270

Ashley I. Pezzner
Registration No. 35,646
Attorney of Record

AIP:ycs

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Description

High-performance membrane electrode unit and the use thereof in fuel cells

The present invention relates to high-performance membrane electrode units, which can particularly be used in so-called polymer electrolyte membrane fuel cells.

A fuel cell usually contains an electrolyte and two electrodes separated by the electrolyte, in which one of the two electrodes is supplied with a fuel, such as hydrogen gas or a mixture of methanol and water, and the other electrode is supplied with an oxidant, such as oxygen gas or air. In the process, chemical energy generated by the resulting fuel oxidation is directly converted into electric power.

One requirement of the electrolyte is that it is permeable to hydrogen ions, i.e. protons, but not to the fuels mentioned above.

Typically, a fuel cell comprises several individual cells, so-called MEUs (membrane electrode unit), each of which contains an electrolyte and two electrodes separated by the electrolyte.

As electrolyte for the fuel cell, solids, such as polymer electrolyte membranes, or liquids, such as phosphoric acid, are applied. Polymer electrolyte membranes have recently attracted interest as electrolytes for fuel cells.

Polymer electrolyte membranes with complexes of alkaline polymers and strong acids are known from WO96/13872, for example. To produce these, an alkaline polymer, for example polybenzimidazole, is treated with a strong acid, such as phosphoric acid.

Furthermore, fuel cells whose membrane comprises inorganic support materials, such as for example glass-fibre fabrics or glass-fibre veils, which are saturated with phosphoric acid, are also known, for example from US-A-4,017,664.

In the alkaline polymer membranes known in the prior art, the mineral acid (mostly concentrated phosphoric acid) used - to achieve the required proton conductivity - is usually added following the forming of the polyazole film. In doing so, the polymer serves as a support for the electrolyte consisting of the highly concentrated phosphoric acid. In the process, the polymer membrane fulfils further essential

functions, particularly, it has to exhibit a high mechanical stability and serve as a separator for the two fuels mentioned at the outset.

An essential advantage of such a membrane doped with phosphoric acid is the fact that a fuel cell in which such a polymer electrolyte membrane is employed can be operated at temperatures above 100°C without the humidification of the fuels otherwise neçessary. This is due to the characteristic of the phosphoric acid to be able to transport the protons without additional water via the so-called Grotthus mechanism (K.-D. Kreuer, Chem. Mater. 1996, 8, 610-641).

Further advantages for the fuel cell system are achieved through the possibility of operation at temperatures above 100°C. On the one hand, the sensitivity of the Pt catalyst to gas impurities, in particular CO, is reduced substantially. CO is formed as a by-product in the reforming of hydrogen-rich gas from carbon-containing compounds, such as e.g. natural gas, methanol or benzine, or also as an intermediate product in the direct oxidation of methanol. Typically, the CO content of the fuel has to be lower than 100 ppm at temperatures <100°C. However, at temperatures in the range of from 150-200°, 10,000 ppm CO or more can also be tolerated (N. J. Bjerrum et. al., Journal of Applied Electrochemistry, 2001, 31, 773-779). This results in substantial simplifications of the upstream reforming process and therefore reductions of the cost of the entire fuel cell system.

The output of a membrane electrode unit produced with such membranes is described in WO 01/18894 and in Electrochimica Acta, Volume 41, 1996, 193-197 and amounts to less than 0.2 A/cm² with a platinum loading of 0.5 mg/cm² (anode) and 2 mg/cm² (cathode) and a voltage of 0.6 V. When using air instead of oxygen, this value drops to less than 0.1 A/cm².

A big advantage of fuel cells is the fact that, in the electrochemical reaction, the energy of the fuel is directly converted into electric power and heat. In the process, water is formed at the cathode as a reaction product. Heat is also produced in the electrochemical reaction as a by-product. In applications in which only the power for the operation of electric motors is utilised, such as e.g. in automotive applications, or as a versatile replacement of battery systems, part of the heat generated in the reaction has to be dissipated to prevent overheating of the system. Additional energy-consuming devices which further reduce the total electric efficiency of the fuel cell are then needed for cooling. In stationary applications, such as for the centralised or decentralised generation of electricity and heat, the heat can be used efficiently by

existing technologies, such as e.g. heat exchangers. In doing so, high temperatures are aimed for to increase the efficiency. If the operating temperature is higher than 100°C and the temperature difference between the ambient temperature and the operating temperature is high, it will be possible to cool the fuel cell system more efficiently, for example using smaller cooling surfaces and dispensing with additional devices, in comparison to fuel cells which have to be operated at less than 100°C due to the humidification of the membrane.

The membrane electrode units set forth above already show a good property profile, however, the capability, for example the current density at high voltages, of known membrane electrode units has to be improved further.

A further object was to provide a membrane electrode unit which exhibits a high capability, in particular a high current density or a high current density at a high voltage, respectively, over a wide range of temperatures.

Additionally, the membrane electrode unit according to the invention has to display high durability, in particular a long service life at the high power densities demanded.

An ongoing object in all membrane electrode units is to lower the quantities of catalysts to minimise the production costs without thereby reducing the capability significantly. Advantageously, it should be possible to operate the membrane electrode unit with little gas flow and/or with low excess pressure achieving high power density.

Therefore, the present invention has the object to provide a novel membrane electrode unit which solves the objects set forth above.

The object of the present invention is a membrane electrode unit comprising

A) at least one polymer membrane which includes at least one polymer with at least one nitrogen atom, the polymer membrane including at least one mineral acid,

B) at least two electrodes,

characterized in that at least one electrode comprises a catalyst containing

i. at least one precious metal of the platinum group, in particular Pt, Pd, Ir, Rh, Os, Ru, and/or at least one precious metal Au and/or Ag

ii. at least one metal less precious according to the electrochemical series as the metal mentioned in (i.), in particular selected from the group of Fe, Co, Ni, Cr, Mn, Zr, Ti, Ga, V

The membrane electrode unit according to the invention provides high current intensities without the voltage being lowered too much. The membrane electrode units further exhibit good durability at high current intensities.

A fundamental aspect and technical advantage of the membrane electrode unit according to the invention is that the excellent capability is obtained with a low concentration of catalytically active substances, such as for example platinum, ruthenium or palladium, heretofore not achieved.

The polymers which comprise at least one nitrogen atom are formed in the polymer membrane included in the membrane electrode unit according to the invention. These polymers are also called alkaline polymers. The alkalinity of the polymer can also be defined via the molar ratio of nitrogen atoms to carbon atoms. The scope of the present invention encompasses in particular such polymers whose molar ratio of nitrogen atoms to carbon atoms is in the range of from 1:1 to 1:100, preferably in the range of from 1:2 to 1:20. This ratio can be determined by elemental analysis.

Alkaline polymers, in particular polymers with at least one nitrogen atom, are known in professional circles. In general, polymers with one nitrogen atom in the backbone and/or in the side chain can be used.

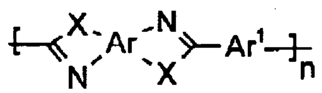
The polymers with one nitrogen atom include, for example, polyphosphazenes, polyimines, polyisocyanides, polyetherimine, polyaniline, polyamides, polyhydrazides, polyurethanes, polyimides, polyazoles and/or polyazines.

Preferably, the polymer membranes comprise polymers with at least one nitrogen atom used in a repeating unit. In this connection, it is also possible to use copolymers which, in addition to repeating units with one nitrogen atom, also comprise repeating units without a nitrogen atom.

According to a particular aspect of the present invention, alkaline polymers with at least one nitrogen atom are used. The term alkaline is known in professional circles in which this is to be understood in particular as Lewis and Brønstedt alkalinity.

The repeating unit in the alkaline polymer preferably contains an aromatic ring with at least one nitrogen atom. The aromatic ring is preferably a five- to six-membered ring with one to three nitrogen atoms which can be fused to another ring, in particular another aromatic ring.

Polymers based on polyazole generally contain recurring azole units of the general formula (I) and/or (II) and/or (III) and/or (IV) and/or (V) and/or (VI) and/or (VII) and/or (VIII) and/or (IX) and/or (X) and/or (XI) and/or (XII) and/or (XIII) and/or (XIV) and/or (XV) and/or (XVI) and/or (XVII) and/or (XVIII) and/or (XIX) and/or (XX) and/or (XXI) and/or (XXII).



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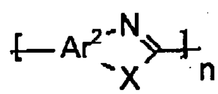

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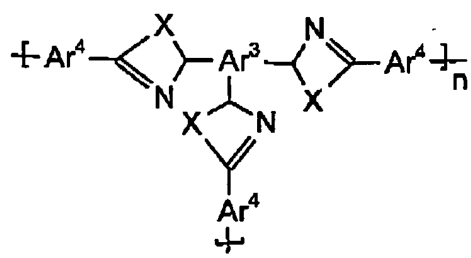

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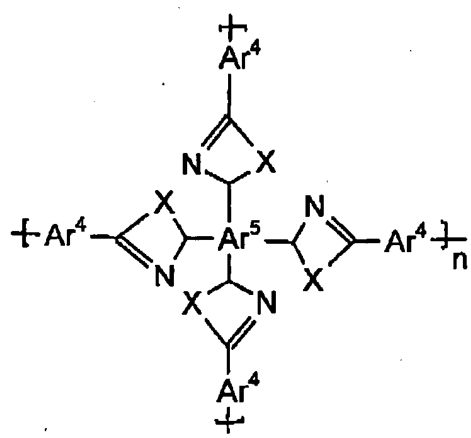

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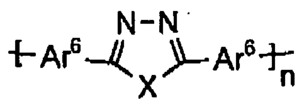

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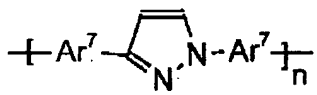

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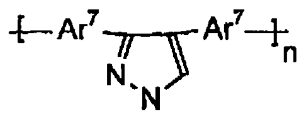

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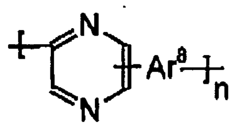

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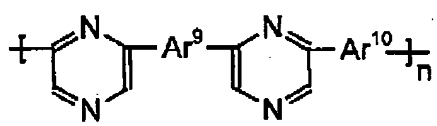

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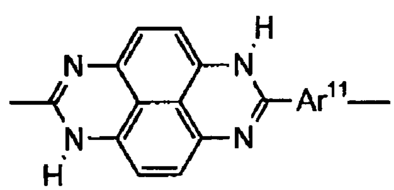

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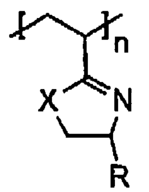

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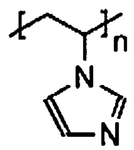

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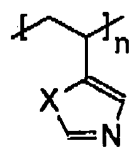

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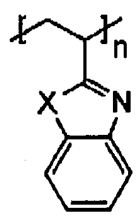

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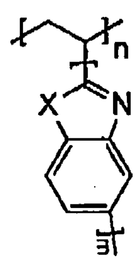

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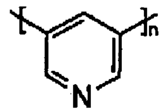

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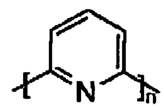

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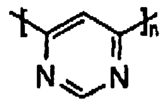

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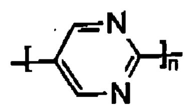

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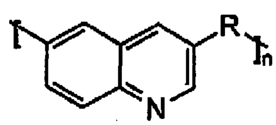

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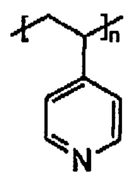
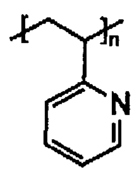


(XXI)



(XXII)

wherein

Ar are identical or different and represent a tetracovalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,

Ar^1 are identical or different and represent a bicovalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,

Ar^2 are identical or different and represent a bicovalent or tricovalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,

Ar^3 are identical or different and represent a tricovalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,

Ar^4 are identical or different and represent a tricovalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,

Ar^5 are identical or different and represent a tetracovalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,

Ar^6 are identical or different and represent a bicovalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,

Ar^7 are identical or different and represent a bicovalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,

Ar^8 are identical or different and represent a tricovalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,

Ar^9 are identical or different and represent a bicovalent or tricovalent or tetracovalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,

Ar^{10} are identical or different and represent a bicovalent or tricovalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,

Ar^{11} are identical or different and represent a bicovalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,

X are identical or different and represent oxygen, sulphur or an amino group which carries a hydrogen atom, a group having 1 - 20 carbon atoms, preferably a branched or unbranched alkyl or alkoxy group, or an aryl group as a further radical,

R are identical or different and represent hydrogen, an alkyl group and an aromatic group, with the proviso that R in the formula (XX) is not hydrogen, and

n, m are each an integer greater than or equal to 10, preferably greater or equal to 100.

Aromatic or heteroaromatic groups preferred according to the invention are derived from benzene, naphthalene, biphenyl, diphenyl ether, diphenylmethane,

diphenyldimethylmethane, bisphenone, diphenylsulphone, thiophene, furan, pyrrole, thiazole, oxazole, imidazole, isothiazole, isoxazole, pyrazole, 1,3,4-oxadiazole, 2,5-diphenyl-1,3,4-oxadiazole, 1,3,4-thiadiazole, 1,3,4-triazole, 2,5-diphenyl-1,3,4-triazole, 1,2,5-triphenyl-1,3,4-triazole, 1,2,4-oxadiazole, 1,2,4-thiadiazole, 1,2,4-triazole, 1,2,3-triazole, 1,2,3,4-tetrazole, benzo[b]thiophene, benzo[b]furan, indole, benzo[c]thiophene, benzo[c]furan, isoindole, benzoxazole, benzothiazole, benzimidazole, benzisoxazole, benzisothiazole, benzopyrazole, benzothiadiazole, benzotriazole, dibenzofuran, dibenzothiophene, carbazole, pyridine, bipyridine, pyrazine, pyrazole, pyrimidine, pyridazine, 1,3,5-triazine, 1,2,4-triazine, 1,2,4,5-triazine, tetrazine, quinoline, isoquinoline, quinoxaline, quinazoline, cinnoline, 1,8-naphthyridine, 1,5-naphthyridine, 1,6-naphthyridine, 1,7-naphthyridine, phthalazine, pyridopyrimidine, purine, pteridine or quinolizine, 4H-quinolizine, diphenyl ether, anthracene, benzopyrrole, benzooxathiadiazole, benzooxadiazole, benzopyridine, benzopyrazine, benzopyrazidine, benzopyrimidine, benzotriazine, indolizine, pyridopyridine, imidazopyrimidine, pyrazinopyrimidine, carbazole, aziridine, phenazine, benzoquinoline, phenoxazine, phenothiazine, acridizine, benzopteridine, phenanthroline and phenanthrene which optionally also can be substituted.

In this case, Ar^1, Ar^4, Ar^6, Ar^7, Ar^8, Ar^9, Ar^{10}, Ar^{11} can have any substitution pattern, in the case of phenylene, for example, Ar^1, Ar^4, Ar^6, Ar^7, Ar^8, Ar^9, Ar^{10}, Ar^{11} can be ortho-, meta- and para-phenylene. Particularly preferred groups are derived from benzene and biphenylene which optionally also can be substituted.

Preferred alkyl groups are short-chain alkyl groups having 1 to 4 carbon atoms, e.g. methyl, ethyl, n- or i-propyl and t-butyl groups.

Preferred aromatic groups are phenyl or naphthyl groups. The alkyl groups and the aromatic groups can be substituted.

Preferred substituents are halogen atoms, e.g. fluorine, amino groups, hydroxy groups or short-chain alkyl groups, e.g. methyl or ethyl groups.

Polyazoles having recurring units of the formula (I) are preferred wherein the radicals X within one recurring unit are identical.

The polyazoles can in principle also have different recurring units wherein their radicals X are different, for example. It is preferable, however, that a recurring unit has only identical radicals X.

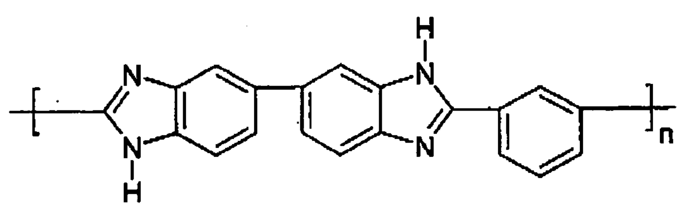
Further preferred polyazole polymers are polyimidazoles, polybenzothiazoles, polybenzoxazoles, polyoxadiazoles, polyquinoxalines, polythiadiazoles, poly(pyridines), poly(pyrimidines) and poly(tetrazapyrenes).

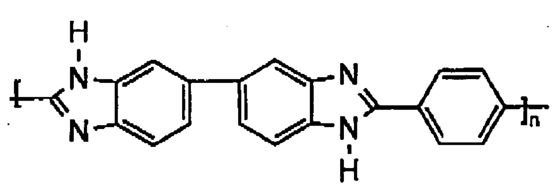
In another embodiment of the present invention, the polymer containing recurring azole units is a copolymer or a blend which contains at least two units of the formulae (I) to (XXII) which differ from one another. The polymers can be in the form of block copolymers (diblock, triblock), random copolymers, periodic copolymers and/or alternating polymers.

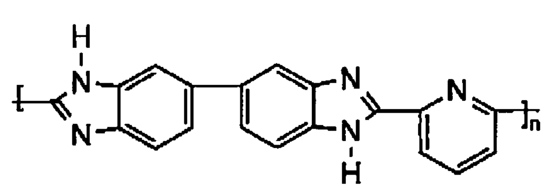
In a particularly preferred embodiment of the present invention, the polymer containing recurring azole units is a polyazole which only contains units of the formulae (I) and/or (II).

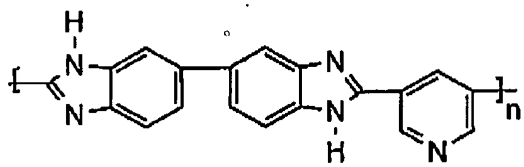
The number of recurring azole units in the polymer is preferably an integer greater than or equal to 10. Particularly preferred polymers contain at least 100 recurring azole units.

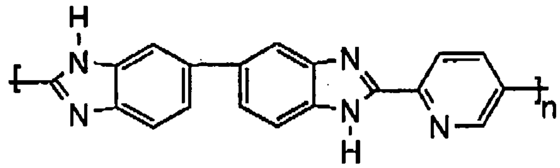
Within the scope of the present invention, polymers containing recurring benzimidazole units are preferred. Some examples of the most appropriate polymers containing recurring benzimidazole units are represented by the following formulae:

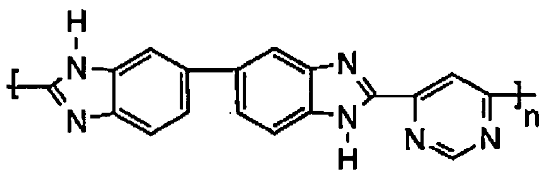


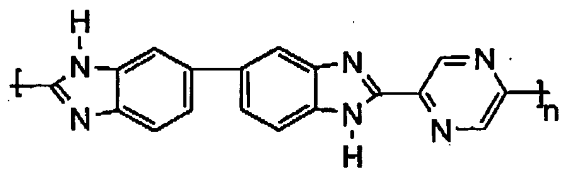


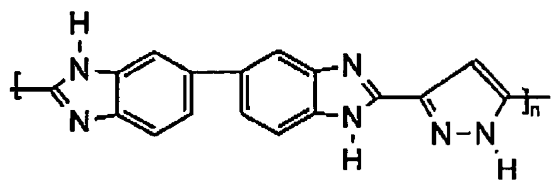


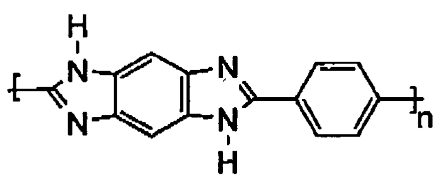


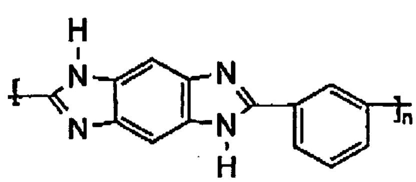


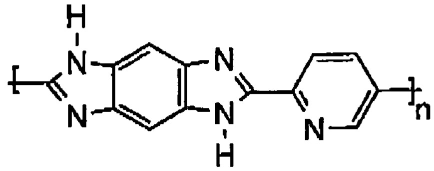


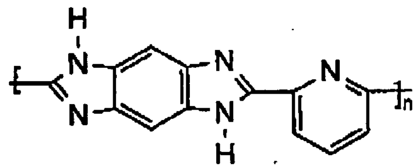


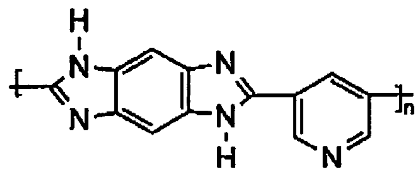


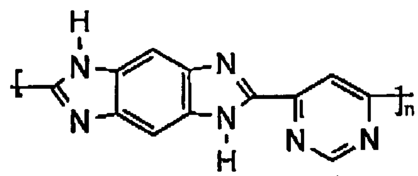


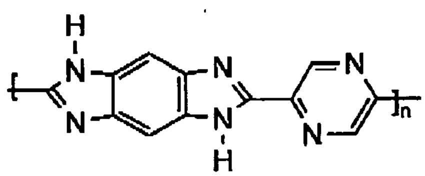


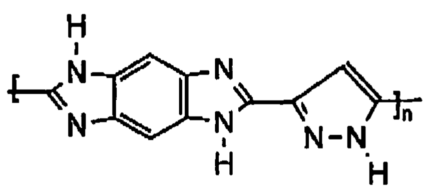


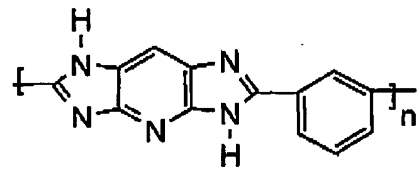


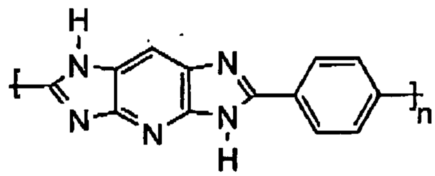


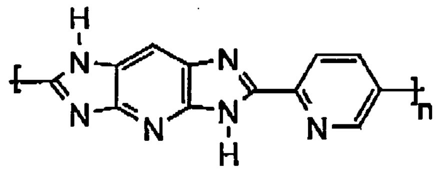


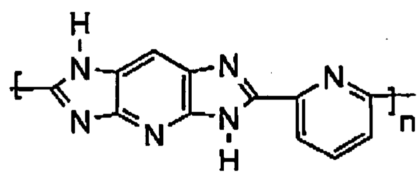


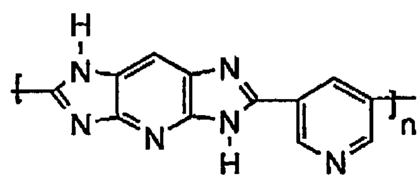


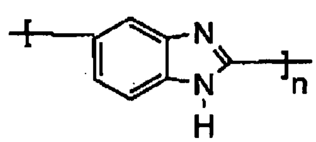


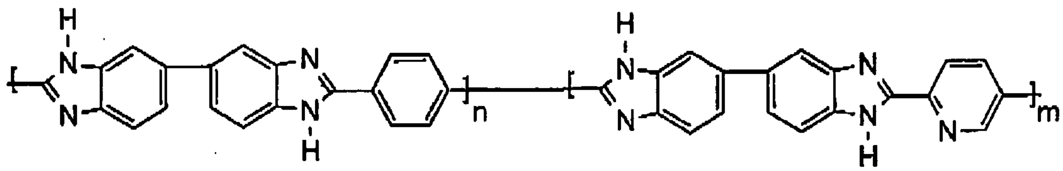


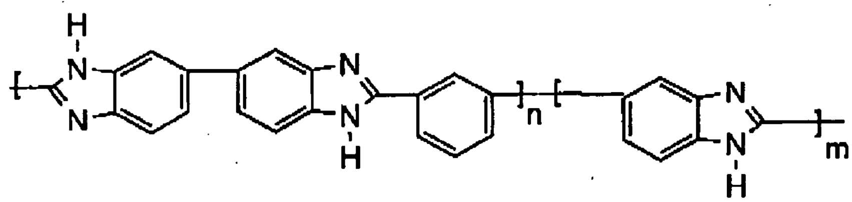












wherein n and m are each an integer greater than or equal to 10, preferably greater than or equal to 100.

Further preferred polyazole polymers are polyimidazoles, polybenzimidazole ether ketone, polybenzothiazoles, polybenzoxazoles, polytriazoles, polyoxadiazoles, polythiadiazoles, polypyrazoles, polyquinoxalines, poly(pyridines), poly(pyrimidines) and poly(tetrazapyrenes).

Preferred polyazoles are characterized by a high molecular weight. This applies in particular to the polybenzimidazoles. Measured as the intrinsic viscosity, this is in the range of from 0.3 to 10 dl/g, preferably 1 to 5 dl/g.

Celazole from the company Celanese is particularly preferred. The properties of polymer film and polymer membrane can be improved by screening the starting polymer, as described in German patent application No. 10129458.1.

Very particular preference is given to using para-polybenzimidazoles in the production of the polymer electrolyte membranes. In this connection, the polybenzimidazoles comprise in particular six-membered aromatic groups which are linked at the 1,4 position. Particular preference is given to using poly-[2,2'-(p-phenylene)-5,5'-bisbenzimidazole].

The polymer film used for the doping and based on alkaline polymers can comprise still more additives in the form of fillers and/or auxiliaries. Additionally, the polymer film can feature further modifications, for example by cross-linking, as described in German patent application No. 1010752.8 or in WO 00/44816. In a preferred

embodiment, the polymer film used for the doping and consisting of an alkaline polymer and at least one blend component additionally contains a cross-linking agent, as described in German patent application No. 10140147.7. An essential advantage of such a system is the fact that higher doping levels and therefore a greater conductivity with sufficient mechanical stability of the membrane can be achieved.

In addition to the above-mentioned alkaline polymers, a blend of one or more alkaline polymers with another polymer can be used. In this case, the function of the blend component is essentially to improve the mechanical properties and reduce the cost of material. Here, polyethersulphone is a preferred blend component, as described in German patent application No. 10052242.4.

The preferred polymers which can be employed as the blend component include, amongst others, polyolefines, such as poly(chloroprene), polyacetylene, polyphenylene, poly(*p*-xylylene), polyarylmethylene, polyarmethylene, polystyrene, polymethylstyrene, polyvinyl alcohol, polyvinyl acetate, polyvinyl ether, polyvinyl amine, poly(N-vinyl acetamide), polyvinyl imidazole, polyvinyl carbazole, polyvinyl pyrrolidone, polyvinyl pyridine, polyvinyl chloride, polyvinylidene chloride, polytetrafluoroethylene, polyhexafluoropropylene, copolymers of PTFE with hexafluoropropylene, with perfluoropropylvinyl ether, with trifluoronitrosomethane, with sulphonyl fluoride vinyl ether, with carbalkoxyperfluoroalkoxyvinyl ether, polychlorotrifluoroethylene, polyvinyl fluoride, polyvinylidene fluoride, polyacrolein, polyacrylamide, polyacrylonitrile, polycyanoacrylates, polymethacrylimide, cycloolefinic copolymers, in particular of norbornenes;
polymers having C-O bonds in the backbone, for example polyacetal, polyoxymethylene, polyether, polypropylene oxide, polyepichlorohydrin, polytetrahydrofuran, polyphenylene oxide, polyether ketone, polyester, in particular polyhydroxyacetic acid, polyethyleneterephthalate, polybutyleneterephthalate, polyhydroxybenzoate, polyhydroxypropionic acid, polypivalolacton, polycaprolacton, polymalonic acid, polycarbonate;
polymer with C-S bonds in the backbone, for example polysulphide ether, polyphenylenesulphide, polyethersulphone;
polymer with C-N bonds in the backbone, for example polyimines, polyisocyanides, polyetherimine, polyaniline, polyamides, polyhydrazides, polyurethanes, polyimides, polyazoles, polyazines;
liquid crystalline polymers, in particular Vectra, as well as

inorganic polymers, such as polysilanes, polycarbosilanes, polysiloxanes, polysilicic acid, polysilicates, silicons, polyphosphazenes and polythiazyl.

For the application in fuel cells with a long-term service temperature above 100°C, such blend polymers that have a glass transition temperature or Vicat softening point VST/A/50 of at least 100°C, preferably at least 150°C and very particularly preferably at least 180°C, are preferred. In this connection, polysulphones with a Vicat softening point VST/A/50 of from 180°C to 230°C are preferred.

The preferred polymers include polysulphones, in particular polysulphone having aromatic groups in the backbone. According to a particular aspect of the present invention, preferred polysulphones and polyethersulphones have a melt volume rate MVR 300/21.6 of less than or equal to 40 cm^3/10 min, in particular less than or equal to 30 cm^3/10 min and particularly preferably less than or equal to 20 cm^3/10 min, measured in accordance with ISO 1133.

According to a particular aspect, the polymer membrane can comprise at least one polymer with aromatic sulphonic acid groups. Aromatic sulphonic acid groups are groups in which the sulphonic acid groups ($-SO_3H$) are bound covalently to an aromatic or heteroaromatic group. The aromatic group can be part of the backbone of the polymer or part of a side group wherein polymers having aromatic groups in the backbone are preferred. In many cases, the sulphonic acid groups can also be employed in the form of their salts. Furthermore, derivatives, for example esters, in particular methyl or ethyl esters, or halides of the sulphonic acids can be used which are converted to the sulphonic acid during operation of the membrane.

Preferred aromatic or heteroaromatic groups are derived from benzene, naphthalene, biphenyl, diphenyl ether, diphenylmethane, diphenyldimethylmethane, bisphenone, diphenylsulphone, thiophene, furan, pyrrole, thiazole, oxazole, imidazole, isothiazole, isoxazole, pyrazole, 1,3,4-oxadiazole, 2,5-diphenyl-1,3,4-oxadiazole, 1,3,4-thiadiazole, 1,3,4-triazole, 2,5-diphenyl-1,3,4-triazole, 1,2,5-triphenyl-1,3,4-triazole, 1,2,4-oxadiazole, 1,2,4-thiadiazole, 1,2,4-triazole, 1,2,3-triazole, 1,2,3,4-tetrazole, benzo[b]thiophene, benzo[b]furan, indole, benzo[c]thiophene, benzo[c]furan, isoindole, benzoxazole, benzothiazole, benzimidazole, benzisoxazole, benzisothiazole, benzopyrazole, benzothiadiazole, benzotriazole, dibenzofuran, dibenzothiophene, carbazole, pyridine, bipyridine, pyrazine, pyrazole, pyrimidine, pyridazine, 1,3,5-triazine, 1,2,4-triazine, 1,2,4,5-triazine, tetrazine, quinoline, isoquinoline, quinoxaline, quinazoline, cinnoline, 1,8-naphthyridine, 1,5-

naphthyridine, 1,6-naphthyridine, 1,7-naphthyridine, phthalazine, pyridopyrimidine, purine, pteridine or quinolizine, 4H-quinolizine, diphenyl ether, anthracene, benzopyrrole, benzooxathiadiazole, benzooxadiazole, benzopyridine, benzopyrazine, benzopyrazidine, benzopyrimidine, benzotriazine, indolizine, pyridopyridine, imidazopyrimidine, pyrazinopyrimidine, carbazole, aziridine, phenazine, benzoquinoline, phenoxazine, phenothiazine, acridizine, benzopteridine, phenanthroline and phenanthrene which optionally also can be substituted. Preferred substituents are halogen atoms, such as e.g. fluorine, amino groups, hydroxy groups or alkyl groups.

In this case, the substitution pattern can be in any form, in the case of phenylene, for example, it can be ortho-, meta- and para-phenylene. Particularly preferred groups are derived from benzene and biphenylene which optionally also can be substituted.

Preferred alkyl groups are short-chain alkyl groups having 1 to 4 carbon atoms, e.g. methyl, ethyl, n- or i-propyl and t-butyl groups.

Preferred aromatic groups are phenyl or naphthyl groups. The alkyl groups and the aromatic groups can be substituted.

The polymers modified with sulphonic acid groups preferably have a content of sulphonic acid groups in the range of from 0.5 to 3 meq/g, preferably 0.5 to 2 meq/g. This value is determined through the so-called ion exchange capacity (IEC).

To measure the IEC, the sulphonic acid groups are converted to the free acid. To this end, the polymer is treated in a known way with acid, removing excess acid by washing. Thus, the sulphonated polymer is initially treated for 2 hours in boiling water. Subsequently, excess water is dabbed off and the sample is dried at 160°C in a vacuum drying cabinet at $p < 1$ mbar for 15 hours. Then, the dry weight of the membrane is determined. The polymer thus dried is then dissolved in DMSO at 80°C for 1 h. Subsequently, the solution is titrated with 0.1M NaOH. The ion exchange capacity (IEC) is then calculated from the consumption of acid to reach the equivalence point and from the dry weight.

Polymers with sulphonic acid groups covalently bound to aromatic groups are known in professional circles. Polymers with aromatic sulphonic acid groups can, for example, be produced by sulphonation of polymers. Processes for the sulphonation of polymers are described in F. Kucera et al., Polymer Engineering and Science

1988, Vol. 38, No. 5, 783-792. In this connection, the sulphonation conditions can be chosen such that a low degree of sulphonation develops (DE-A-19959289).

With regard to polymers having aromatic sulphonic acid groups whose aromatic radicals are part of the side group, particular reference shall be made to polystyrene derivatives. The document US-A-6110616 for instance describes copolymers of butadiene and styrene and their subsequent sulphonation for use in fuel cells.

Furthermore, such polymers can also be obtained by polyreactions of monomers which comprise acid groups. Thus, perfluorinated polymers as described in US-A-5422411 can be produced by copolymerisation of trifluorostyrene and sulphonyl-modified trifluorostyrene.

According to a particular aspect of the present invention, thermoplastics stable at high temperatures which include sulphonic acid groups bound to aromatic groups are employed. In general, such polymers have aromatic groups in the backbone. Thus, sulphonated polyether ketones (DE-A-4219077, WO96/01177), sulphonated polysulphones (J. Membr. Sci. 83 (1993), p. 211) or sulphonated polyphenylenesulphide (DE-A-19527435) are preferred.

The polymers set forth above which have sulphonic acid groups bound to aromatic groups can be used individually or as a mixture wherein mixtures having polymers with aromatic groups in the backbone are particularly preferred.

The molecular weight of the polymers having sulphonic acid groups bound to aromatic groups can vary widely, depending on the type of polymer and its processibility. Preferably, the weight average of the molecular weight M_w is in the range of from 5000 to 10,000,000, in particular 10,000 to 1,000,000, particularly preferably 15,000 to 50,000. According to a particular aspect of the present invention, polymers with sulphonic acid groups bound to aromatic groups which have a low polydispersity index M_w/M_n are used. Preferably, the polydispersity index is in the range of from 1 to 5, in particular 1 to 4.

To further improve the properties in terms of application technology, the flat material can feature fillers, in particular proton-conducting fillers.

Non-limiting examples of proton-conducting fillers are

sulphates, such as $CsHSO_4$, $Fe(SO_4)_2$, $(NH_4)_3H(SO_4)_2$, $LiHSO_4$, $NaHSO_4$, $KHSO_4$, $RbSO_4$, $LiN_2H_5SO_4$, NH_4HSO_4,

phosphates, such as $Zr_3(PO_4)_4$, $Zr(HPO_4)_2$, $HZr_2(PO_4)_3$, $UO_2PO_4.3H_2O$, $H_8UO_2PO_4$, $Ce(HPO_4)_2$, $Ti(HPO_4)_2$, KH_2PO_4, NaH_2PO_4, LiH_2PO_4, $NH_4H_2PO_4$, CsH_2PO_4, $CaHPO_4$, $MgHPO_4$, $HSbP_2O_8$, $HSb_3P_2O_{14}$, $H_5Sb_5P_2O_{20}$,

polyacid, such as $H_3PW_{12}O_{40}.nH_2O$ (n=21-29), $H_3SiW_{12}O_{40}.nH_2O$ (n=21-29), H_xWO_3, $HSbWO_6$, $H_3PMo_{12}O_{40}$, $H_2Sb_4O_{11}$, $HTaWO_6$, $HNbO_3$, $HTiNbO_5$, $HTiTaO_5$, $HSbTeO_6$, $H_5Ti_4O_9$, $HSbO_3$, H_2MoO_4

selenites and arsenides, such as $(NH_4)_3H(SeO_4)_2$, UO_2AsO_4, $(NH_4)_3H(SeO_4)_2$, KH_2AsO_4, $Cs_3H(SeO_4)_2$, $Rb_3H(SeO_4)_2$,

phosphides, such as ZrP, TiP, HfP

oxides, such as Al_2O_3, Sb_2O_5, ThO_2, SnO_2, ZrO_2, MoO_3

silicates, such as zeolites, zeolites(NH_4+), phyllosilicates, tectosilicates, H-natrolites, H-mordenites, NH_4-analcines, NH_4-sodalites, NH_4-gallates, H-montmorillonites

acids, such as $HClO_4$, SbF_5

fillers, such as carbides, in particular SiC, Si_3N_4, fibres, in particular glass fibres, glass powders and/or polymer fibres, preferably based on polyazoles.

These additives can be included in the proton-conducting polymer membrane in usual amounts, however, the positive properties of the membrane, such as great conductivity, long service life and high mechanical stability, should not be affected too much by the addition of too large amounts of additives. Generally, the membrane comprises not more than 80% by weight, preferably not more than 50% by weight and particularly preferably not more than 20% by weight, of additives.

To produce the polymer film, the polymer components are initially dissolved or suspended, as described in the applications cited above, for example DE No. 10110752.8 or WO 00/44816, and subsequently used for the production of the polymer films. Furthermore, the polymer films in accordance with DE No. 10052237.8 can be produced continuously.

Alternatively, the formation of the film can take place in accordance with the process described in the Japanese application No. Hei 10-125560.

In this, the solution is poured into a cylinder with a cylindrical interior surface and the cylinder is then set into rotation. At the same time, the solvent is allowed to evaporate via the centrifugal force caused by the rotation, thereby forming a cylindrical polymer film on the interior surface of the cylinder wherein the film has a thickness that is largely uniform.

With this process, the alkaline polymer having a uniform matrix can be formed. This process described in the Japanese patent application Hei 10-125560 is also part of the present description.

Then, the solvent is removed. This can take place by methods known to the person skilled in the art, for example by drying.
The film made of alkaline polymer or polymer blend is subsequently impregnated or doped with a strong acid, preferably a mineral acid, wherein the film can be treated as described previously in the German patent application No. 10109829.4. This variant is beneficial to exclude interactions of the residual solvent with the barrier layer.

To this end, the film comprising at least one polymer with at least one nitrogen atom is immersed in a strong acid such that the film is impregnated with the strong acid and becomes a proton-conducting membrane. For this, the preferably alkaline polymer is usually immersed in a highly concentrated strong acid at a temperature of at least 35°C for a period of time of from several minutes up to several hours.

Mineral acid, in particular phosphoric acid and/or sulphuric acid, is used as the strong acid.

Within the scope of the present description, "phosphoric acid" means polyphosphoric acid ($H_{n+2}P_nO_{3n+1}$ (n>1), which usually has a content of at least 83%, calculated as P_2O_5 (by acidimetry), phosphonic acid (H_3PO_3), orthophosphoric acid (H_3PO_4), pyrophosphoric acid ($H_4P_2O_7$), triphosphoric acid ($H_5P_3O_{10}$) and metaphosphoric acid. The phosphoric acid, in particular orthophosphoric acid, preferably has a concentration of at least 80 percent by weight, particularly preferably a concentration of at least 85 percent by weight, even more preferably a concentration of at least 87 percent by weight and very particularly preferably a concentration of at least 89 percent by weight. It is to be understood that the reason for this is that the preferably alkaline polymer can be impregnated with a greater number of molecules of the strong acid at an increasing concentration of the strong acid.

The obtained polymer electrolyte membrane is proton-conducting. After the doping, the degree of doping should be, expressed as mole of acid per repeating unit, greater than 6, preferably greater than 8 and very particularly preferably greater than 9.

Instead of the polymer membranes based on preferably alkaline polymers and produced by classical processes, it is also possible to use the polyazole-containing polymer membranes, as described in the German patent applications No. 10117686.4, 10144815.5, 10117687.2. Such polymer electrolyte membranes provided with at least one barrier layer are also an object of the present invention.

Polymer membranes can preferably be obtained by a process comprising the steps of

i) preparation of a mixture comprising
   polyphosphoric acid,
   at least one polyazole and/or at least one or more compounds which are suitable for the formation of polyazoles with action of heat in accordance with step ii),
ii) heating the mixture obtainable in accordance with step i) under inert gas to temperatures of up to 400°C,
iii) applying a layer using the mixture in accordance with step i) and/or ii) to a support,
iv) treatment of the membrane formed in step iii).

To this end, one or more compounds can be added to the mixture in accordance with step i), which are suitable for the formation of polyazoles with action of heat in accordance with step ii).

For this, mixtures are suitable which comprise one or more aromatic and/or heteroaromatic tetraamino compounds and one or more aromatic and/or heteroaromatic carboxylic acids or their derivatives, which comprise at least two acid groups per carboxylic acid monomer. Furthermore, one or more aromatic and/or heteroaromatic diaminocarboxylic acids can be used for the preparation of polyazoles.

The aromatic and heteroaromatic tetraamino compounds include, amongst others, 3,3',4,4'-tetraaminobiphenyl, 2,3,5,6-tetraaminopyridine, 1,2,4,5-tetraaminobenzene, 3,3',4,4'-tetraaminodiphenyl sulphone, 3,3',4,4'-tetraaminodiphenyl ether, 3,3',4,4'-

tetraaminobenzophenone, 3,3',4,4'-tetraaminodiphenylmethane and 3,3',4,4'-tetraaminodiphenyldimethylmethane
and their salts, in particular their monohydrochloride, dihydrochloride, trihydrochloride and tetrahydrochloride derivatives. Of these, 3,3',4,4'-tetraaminobiphenyl, 2,3,5,6-tetraaminopyridine and 1,2,4,5-tetraaminobenzene are particularly preferred.

Furthermore, the mixture i) can comprise aromatic and/or heteroaromatic carboxylic acids. These are dicarboxylic acids and tricarboxylic acids and tetracarboxylic acids or their esters or their anhydrides or their acid halides, especially their acid halides and/or acid bromides. Preferably, the aromatic dicarboxylic acids are isophthalic acid, terephthalic acid, phthalic acid, 5-hydroxyisophthalic acid, 4-hydroxyisophthalic acid, 2-hydroxyterephthalic acid, 5-aminoisophthalic acid, 5-N,N-dimethylaminoisophthalic acid, 5-N,N-diethylaminoisophthalic acid, 2,5-dihydroxyterephthalic acid, 2,6-dihydroxyisophthalic acid, 4,6-dihydroxyisophthalic acid, 2,3-dihydroxyphthalic acid, 2,4-dihydroxyphthalic acid, 3,4-dihydroxyphthalic acid, 3-fluorophthalic acid, 5-fluoroisophthalic acid, 2-fluoroterephthalic acid, tetrafluorophthalic acid, tetrafluoroisophthalic acid, tetrafluoroterephthalic acid,1,4-naphthalenedicarboxylic acid, 1,5-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid, diphenic acid, 1,8-dihydroxynaphthalene-3,6-dicarboxylic acid, diphenyl ether-4,4'-dicarboxylic acid, benzophenone-4,4'-dicarboxylic acid, diphenylsulphone-4,4'-dicarboxylic acid, biphenyl-4,4'-dicarboxylic acid, 4-trifluoromethylphthalic acid, 2,2-bis-(4-carboxyphenyl)hexafluoropropane, 4,4'-stilbenedicarboxylic acid, 4-carboxycinnamic acid or their C1-C20 alkyl esters or C5-C12 aryl esters or their acid anhydrides or their acid chlorides.

Very particular preference is given to using mixtures which comprise dicarboxylic acids, the acid radicals of which are in the para position, such as for example terephthalic acid.

The heteroaromatic carboxylic acids are heteroaromatic dicarboxylic acids and tricarboxylic acids and tetracarboxylic acids or their esters or their anhydrides. Heteroaromatic carboxylic acids are understood to mean aromatic systems which contain at least one nitrogen, oxygen, sulphur or phosphorus atom in the aromatic group. Preferably, these are pyridine-2,5-dicarboxylic acid, pyridine-3,5-dicarboxylic acid, pyridine-2,6-dicarboxylic acid, pyridine-2,4-dicarboxylic acid, 4-phenyl-2,5-pyridinedicarboxylic acid, 3,5-pyrazoledicarboxylic acid, 2,6-pyrimidinedicarboxylic acid, 2,5-pyrazinedicarboxylic acid, 2,4,6-pyridinetricarboxylic acid, benzimidazole-

5,6-dicarboxylic acid and their C1-C20 alkyl esters or C5-C12 aryl esters or their acid anhydrides or their acid chlorides.

Furthermore, the mixture i) can also comprise aromatic and heteroaromatic diaminocarboxylic acids. These include, amongst others, diaminobenzoic acid, 4-phenoxycarbonyl-3',4'-diaminodiphenyl ether and their monohydrochloride and dihydrochloride derivatives.

The mixture produced in step i) preferably comprises at least 0.5% by weight, in particular 1 to 30% by weight and particularly preferably 2 to 15% by weight, of monomers for the preparation of polyazoles.

According to another aspect of the present invention, the mixture produced in step i) comprises compounds which are suitable for the formation of polyazoles with action of heat in accordance with step ii), these compounds being obtainable by reaction of one or more aromatic and/or heteroaromatic tetraamino compounds with one or more aromatic and/or heteroaromatic carboxylic acids or their derivatives, which contain at least two acid groups per carboxylic acid monomer, or of one or more aromatic and/or heteroaromatic diaminocarboxylic acids in the melt at temperatures of up to 400°C, in particular up to 350°C, preferably up to 280°C. The compounds to be used for the preparation of these prepolymers were set forth above.

Furthermore, monomers which comprise covalently bound acid groups can be used for the preparation of polyazoles. These include, amongst others, aromatic and heteroaromatic dicarboxylic acids or their derivatives which include at least one phosphonic acid group, for example 2,5-dicarboxyphenylphosphonic acid, 2,3-dicarboxyphenylphosphonic acid, 3,4-dicarboxyphenylphosphonic acid and 3,5-dicarboxyphenylphosphonic acid; aromatic and heteroaromatic dicarboxylic acids or their derivatives which include at least one sulphonic acid group, in particular 2,5-dicarboxyphenylsulphonic acid, 2,3-dicarboxyphenylsulphonic acid, 3,4-dicarboxyphenylsulphonic acid and 3,5-dicarboxyphenylsulphonic acid; aromatic and heteroaromatic diaminocarboxylic acids which comprise at least one phosphonic acid group, for example 2,3-diamino-5-carboxyphenylphosphonic acid, 2,3-diamino-6-carboxyphenylphosphonic acid and 3,4-diamino-6-carboxyphenylphosphonic acid; aromatic and heteroaromatic diaminocarboxylic acids which comprise at least one sulphonic acid group, for example 2,3-diamino-5-carboxyphenylsulphonic acid, 2,3-diamino-6-carboxyphenylsulphonic acid and 3,4-diamino-6-carboxyphenylsulphonic acid.

A polyazole membrane produced in accordance with the process set forth above can include the optional components set forth above. These include in particular blend polymers and fillers. Blend polymers can, amongst other things, be dissolved, dispersed or suspended in the mixture obtained in accordance with step i) and/or step ii). In this connection, the weight ratio of polyazole to polymer (B) is preferably in the range of from 0.1 to 50, preferably from 0.2 to 20, particularly preferably from 1 to 10; however, this should not constitute a limitation. If the polyazole is only formed in step ii), it is possible to arrive at the weight ratio by calculations based on the weight of the monomers for the formation of the polyazole in which the compounds released in the condensation, for example water, are to be taken into account.

To further improve the properties in terms of application technology, fillers, in particular proton-conducting fillers, and additional acids can additionally be added to the membrane. The addition can be performed in step i), step ii) and/or step iii), for example. Furthermore, these additives can also be added after the polymerisation in accordance with step iv), if they are in the form of a liquid. These additives were described above.

The polyphosphoric acid used in step i) is a customary polyphosphoric acid as is available, for example, from Riedel-de Haen. The polyphosphoric acids $H_{n+2}P_nO_{3n+1}$ (n>1) usually have a concentration of at least 83%, calculated as P_2O_5 (by acidimetry). Instead of a solution of the monomers, it is also possible to produce a dispersion/suspension.

The mixture obtained in step i) is, in accordance with step ii), heated to a temperature of up to 400°C, in particular 350°C, preferably up to 280°C, in particular 100°C to 250°C and particularly preferably in the range of from 200°C to 250°C. For this, an inert gas, for example nitrogen, or a noble gas, such as neon, argon, is used.

The mixture produced in step i) and/or step ii) can additionally also contain organic solvents. These can affect the processibility in a positive way. For example, the rheology of the solution can be improved such that this can be more easily extruded or applied with a doctor blade.

The formation of the flat structure in accordance with step iii) is performed by means of measures known per se (pouring, spraying, application with a doctor blade, extrusion) which are known from the prior art of polymer film production. Every

support that is considered as inert under the conditions is suitable as a support. These supports include in particular films made of polyethylene terephthalate (PET), polytetrafluoroethylene (PTFE), polyhexafluoropropylene, copolymers of PTFE with hexafluoropropylene, polyimides, polyphenylenesulphides (PPS) and polypropylene (PP). Furthermore, the formation of the membrane can also be performed directly on the electrode provided with a barrier layer.

The thickness of the flat structure in accordance with step iii) is preferably between 10 and 4000 µm, preferably between 15 and 3500 µm, in particular between 20 and 3000 µm, particularly preferably between 30 and 1500 µm und very particularly preferably between 50 and 1200 µm.

The treatment of the membrane in step iv) is performed in particular at temperatures in the range of from 0°C to 150°C, preferably at temperatures between 10°C and 120°C, in particular between room temperature (20°C) and 90°C, in the presence of moisture or water and/or steam. The treatment is preferably performed at normal pressure, but can also be carried out with action of pressure. It is essential that the treatment takes place in the presence of sufficient moisture whereby the polyphosphoric acid present contributes to the solidification of the membrane by means of partial hydrolysis with formation of low molecular weight polyphosphoric acid and/or phosphoric acid.

The partial hydrolysis of the polyphosphoric acid in step iv) leads to a solidification of the membrane and to a reduction in the layer thickness and the formation of a membrane. The solidified membrane generally has a thickness of between 15 and 3000 µm, preferably 20 and 2000 µm, in particular between 20 and 1500 µm.

The upper temperature limit for the treatment in accordance with step iv) is typically 150°C. With extremely short action of moisture, for example from overheated steam, this steam can also be hotter than 150°C. The duration of the treatment is substantial for the upper limit of the temperature.

The partial hydrolysis (step iv)) can also take place in climatic chambers wherein the hydrolysis can be specifically controlled with defined moisture action. In this connection, the moisture can be specifically set via the temperature or saturation of the surrounding area in contact with it, for example gases such as air, nitrogen, carbon dioxide or other suitable gases, or steam. The duration of the treatment depends on the parameters chosen as aforesaid.

Furthermore, the duration of the treatment depends on the thickness of the membrane.

Typically, the duration of the treatment amounts to a few seconds to minutes, for example with action of overheated steam, or up to whole days, for example in the open air at room temperature and lower relative humidity. Preferably, the duration of the treatment is 10 seconds to 300 hours, in particular 1 minute to 200 hours.

If the partial hydrolysis is performed at room temperature (20°C) with ambient air having a relative humidity of 40-80%, the duration of the treatment is 1 to 200 hours.

The membrane obtained in accordance with step iv) can be formed in such a way that it is self-supporting, i.e. it can be detached from the support without any damage and then directly processed further, if applicable.

The treatment in accordance with step iv) leads to curing of the coating. If the membrane is directly formed on the electrode, the treatment in accordance with step iv) is performed until the coating exhibits a sufficient hardness so that it can be pressed to form a membrane electrode unit. A sufficient hardness is given when a membrane treated accordingly is self-supporting. In many cases, however, a lesser hardness is sufficient. The hardness determined in accordance with DIN 50539 (microhardness measurement) is generally at least 1 mN/mm^2, preferably at least 5 mN/mm^2 and very particularly preferably at least 50 mN/mm^2; however, this should not constitute a limitation.

The concentration and the amount of phosphoric acid and therefore the conductivity of the polymer membrane can be set via the degree of hydrolysis, i.e. the duration, temperature and ambient humidity. The concentration of the phosphoric acid is given as mole of acid per mole of repeating unit of the polymer. Within the scope of the present invention, a concentration (mole of phosphoric acid, based on a repeating unit of the formula (III), i.e. polybenzimidazole) between 13 and 80, in particular between 15 and 80 is preferred. Only with very much difficulty or not at all is it possible to obtain such high degrees of doping (concentrations) by doping polyazoles with commercially available orthophosphoric acid.

Preferred polymer membranes show high proton conductivity. This is at least 0.1 S/cm, preferably at least 0.11 S/cm, in particular at least 0.12 S/cm at temperatures of 120°C.
If the membranes comprise polymers with sulphonic acid groups, the membranes also show high conductivity at a temperature of 70°C. The conductivity depends, amongst other things, on the content of sulphonic acid groups of the membrane. The higher this proportion, the better is the conductivity at low temperatures. In this connection, a membrane according to the invention can be humidified at low temperatures. To this end, for example, the compound employed as the energy source, for example hydrogen, can be provided with a proportion of water. In many cases, however, the water formed by the reaction is sufficient to achieve a humidification.

The specific conductivity is measured by means of impedancy spectroscopy in a 4-pole arrangement in potentiostatic mode and using platinum electrodes (wire, diameter of 0.25 mm). The distance between the current-collecting electrodes is 2 cm. The spectrum obtained is evaluated using a simple model comprised of a parallel arrangement of an ohmic resistance and a capacitor. The cross-section of the specimen of the membrane doped with phosphoric acid is measured immediately before mounting the specimen. To measure the temperature dependency, the measurement cell is brought to the desired temperature in an oven and regulated using a Pt-100 thermocouple arranged in the immediate vicinity of the specimen. After the temperature has been reached, the specimen is kept at this temperature for 10 minutes before beginning the measurement.

A membrane electrode unit according to the invention comprises, in addition to the polymer membrane, at least two electrodes which are each in contact with the membrane.

Generally, the electrode comprises a gas diffusion layer. The gas diffusion layer in general exhibits electron conductivity. Flat, electrically conductive and acid-resistant structures are commonly used for this. These include, for example, carbon-fibre paper, graphitised carbon-fibre paper, carbon-fibre fabric, graphitised carbon-fibre fabric and/or flat structures which were rendered conductive by addition of carbon black.

Furthermore, the electrode includes at least one catalyst layer which comprises

i. at least one precious metal of the platinum group, in particular Pt, Pd, Ir, Rh, Os, Ru, and/or at least one precious metal Au and/or Ag

ii. at least one metal less precious according to the electrochemical series as the metal mentioned in (i.), in particular selected from the group of Fe, Co, Ni, Cr, Mn, Zr, Ti, Ga, V.

Preferably, the catalyst is formed in the form of an alloy of the metals (i) and (ii). In addition to the alloy, further catalytically active substances, in particular precious metals of the platinum group, i.e. Pt, Pd, Ir, Rh, Os, Ru, or also the precious metals Au and Ag, can be used. Furthermore, the oxides of the above-mentioned precious metals and/or non-precious metals can also be employed.

The catalytically active particles which comprise the above-mentioned substances can be employed as metal powder, so-called black precious metal, in particular platinum and/or platinum alloys. Such particles generally have a size in the range of from 5 nm to 200 nm, preferably in the range of from 7 nm to 100 nm.

Furthermore, the metals can also be employed on a support material. Preferably, this support comprises carbon which particularly can be used in the form of carbon black, graphite or graphitised carbon black. Furthermore, electrically conductive metal oxides, such as for example, SnO_x, TiO_x, or phosphates, such as e.g. $FePO_x$, $NbPO_x$, $Zr_y(PO_x)_z$, can be used as support material. In this connection, the indices x, y and z designate the oxygen or metal content of the individual compounds which can lie within a known range as the transition metals can be in different oxidation stages.

The content of these metal particles on a support, based on the total weight of the bond of metal and support, is generally in the range of from 1 to 80% by weight, preferably 5 to 60% by weight and particularly preferably 10 to 50% by weight; however, this should not constitute a limitation. The particle size of the support, in particular the size of the carbon particles, is preferably in the range of from 20 to 100 nm, in particular 30 to 60 nm. The size of the metal particles present thereon is preferably in the range of from 1 to 20 nm, in particular 1 to 10 nm and particularly preferably 2 to 6 nm.

The sizes of the different particles represent mean values and can be determined via transmission electron microscopy or X-ray powder diffractometry.

The catalyst layer has a thickness in the range of from 0.1 to 50 μm.

The membrane electrode unit according to the invention has a catalyst loading of between 0.01 and 20 g/m^2, preferably 0.1 and 10 g/m^2 (sum of all precious metals), based on the surface area of the polymer membrane.

The weight ratio of the precious metals of the platinum group or of Au and/or Ag to the metals less precious according to the electrochemical series is between 1:100 and 100:1.

The catalytically active particles set forth above can generally be obtained commercially.

The preparation of the catalysts is described in US392512, JP06007679A940118 or EP450849A911009, for example.

The catalyst can, amongst other things, be applied to the gas diffusion layer. Subsequently, the gas diffusion layer provided with a catalyst layer can be bonded with a polymer membrane to obtain a membrane electrode unit according to the invention.

Furthermore, the polymer membrane can be provided with a catalyst layer including

i. at least one precious metal of the platinum group, in particular Pt, Pd, Ir, Rh, Os, Ru, and/or at least one precious metal Au and/or Ag
ii. at least one metal less precious according to the electrochemical series as the metal mentioned in (i.), in particular selected from the group of Fe, Co, Ni, Cr, Mn, Zr, Ti, Ga, V.

This membrane can then be bonded with a gas diffusion layer. In this connection, it is also possible to use a gas diffusion layer provided with a catalyst layer. In general, however, a gas diffusion layer which does not comprise any catalyst is sufficient.

To apply at least one catalyst layer to a polymer membrane, several methods can be employed. For example, a support can be used in step iii) which is provided with a coating containing a catalyst to provide the layer formed in step iii) or iv) with a catalyst layer.

In this connection, the membrane can be provided with a catalyst layer on one side or both sides. If the membrane is provided with a catalyst layer only on one side, the opposite side of the membrane has to be pressed together with an electrode which

comprises a catalyst layer. If both sides of the membrane are to be provided with a catalyst layer, the following methods can also be applied in combination to achieve an optimal result.

In the membrane electrode unit according to the invention, the catalysts contained in the electrode or the catalyst layer adjacent to the gas diffusion layer at the side of the cathode and anode differ. In a particularly preferred embodiment of the invention, at least the cathode side comprises a catalyst containing

i. at least one precious metal of the platinum group, in particular Pt, Pd, Ir, Rh, Os, Ru, and/or at least one precious metal Au and/or Ag
ii. at least one metal less precious according to the electrochemical series as the metal mentioned in (i.), in particular selected from the group of Fe, Co, Ni, Cr, Mn, Zr, Ti, Ga, V.

According to the invention, the catalyst layer can be applied by a process in which a catalyst suspension is employed. Additionally, powders which comprise the catalyst can be used.

The catalyst suspension contains a catalytically active substance. These were described above.

Furthermore, the catalyst suspension can contain customary additives. These include, amongst others, fluoropolymers, such as e.g. polytetrafluoroethylene (PTFE), thickeners, in particular water-soluble polymers, such as e.g. cellulose derivatives, polyvinyl alcohol, polyethylene glycol, and surface-active substances.

The surface-active substances include in particular ionic surfactants, for example salts of fatty acids, in particular sodium laurate, potassium oleate; and alkylsulphonic acids, salts of alkylsulphonic acids, in particular sodium perfluorohexanesulphonate, lithium perfluorohexanesulphonate, ammonium perfluorohexanesulphonate, perfluorohexanesulphonic acid, potassium nonafluorobutanesulphonate, as well as non-ionic surfactants, in particular ethoxylated fatty alcohols and polyethylene glycols.

Furthermore, the catalyst suspension can comprise components that are liquid at room temperature. These include, amongst others, organic solvents which can be polar or non-polar, phosphoric acid, polyphosphoric acid and/or water. The catalyst

suspension preferably contains 1 to 99% by weight, in particular 10 to 80% by weight, of liquid components.

The polar organic solvents include in particular alcohols, such as ethanol, propanol and/or butanol.

The organic, non-polar solvents include, amongst others, known thinning agents for thin layers, such as the thinning agent for thin layers 8470 from the company DuPont which comprises oils of turpentine.

Fluoropolymers, in particular tetrafluoroethylene polymers, represent particularly preferred additives. According to a particular embodiment of the present invention, the weight ratio of fluoropolymer to catalyst material comprising at least one precious metal and optionally one or more support materials is greater than 0.1, this ratio preferably lying within the range of from 0.2 to 0.6.

The catalyst suspension can be applied to the membrane by customary processes. Depending on the viscosity of the suspension which can also be in the form of a paste, several methods are known by which the suspension can be applied. Processes for coating films, fabrics, textiles and/or paper, in particular spraying methods and printing processes, such as for example screen and silk screen printing processes, inkjet printing processes, application with rollers, in particular anilox rollers, application with a slit nozzle and application with a doctor blade, are suitable. The corresponding process and the viscosity of the catalyst suspension depend on the hardness of the membrane.

The viscosity can be controlled via the solids content, especially the proportion of catalytically active particles, and the proportion of additives. The viscosity to be adjusted depends on the method of application of the catalyst suspension, the optimal values and the determination thereof being familiar to the person skilled in the art.

Depending on the hardness of the membrane, an improvement of the bond of catalyst and membrane can be effected by heating and/or pressing. Additionally, the bond between membrane and catalyst improves through a treatment in accordance with step iv).

Furthermore, the application of a catalyst layer can be carried out at the same time as the treatment of the membrane in accordance with step iv) until the membrane is self-supporting. This can take place, for example, by applying a catalyst suspension containing water to the flat structure in accordance with step iii). Here, the suspension can be sprayed onto the flat surface in accordance with step iii) in the form of fine droplets. In addition to water, the suspension can also contain further solvents and/or thickeners. Depending on the water content, the curing of the membrane is performed in accordance with step iv). Accordingly, the water content can be within wide ranges. The water content preferably is in the range of from 0.1 to 99, in particular 1 to 95% by weight, based on the catalyst suspension.

According to a particular aspect of the present invention, the catalyst layer is applied by a powder process. In this connection, a catalyst powder is used which can contain additional additives which were exemplified above.

To apply the catalyst powder, spraying processes and screening processes, amongst others, can be employed. In the spraying process, the powder mixture is sprayed onto the membrane via a nozzle, for example a slit nozzle. Generally, the membrane provided with a catalyst layer is subsequently heated to improve the bond between catalyst and membrane. The heating process can be performed via a hot roller, for example. Such methods and devices for applying the powder are described in DE 195 09 748, DE 195 09 749 and DE 197 57 492, amongst others.

In the screening process, the catalyst powder is applied to the membrane by a vibrating screen. A device for applying a catalyst powder to a membrane is described in WO 00/26982. After applying the catalyst powder, the bond of catalyst and membrane can be improved by heating and/or the step iv). In this connection, the membrane provided with at least one catalyst layer can be heated to a temperature in the range of from 50 to 200°C, in particular 100 to 180°C.

Furthermore, the catalyst layer can be applied by a process in which a coating containing a catalyst is applied to a support and the coating containing a catalyst and present on the support is subsequently transferred to a polymer membrane. As an example, such a process is described in WO 92/15121.

The support provided with a catalyst coating can be produced, for example, by preparing a catalyst suspension described above. This catalyst suspension is then

applied to a backing film, for example made of polytetrafluoroethylene. After applying the suspension, the volatile components are removed.

The transfer of the coating containing a catalyst can be performed by hot pressing, amongst others. To this end, the composite comprising a catalyst layer and a membrane as well as a backing film is heated to a temperature in the range of from 50°C to 200°C and pressed together with a pressure of 0.1 to 5 MPa. In general, a few seconds are sufficient to join the catalyst layer to the membrane. Preferably, this period of time is in the range of from 1 second to 5 minutes, in particular 5 seconds to 1 minute.
According to a particular embodiment of the present invention, the catalyst layer has a thickness in the range of from 1 to 1000 µm, in particular from 5 to 500, preferably from 10 to 300 µm. This value represents a mean value which can be determined by averaging the measurements of the layer thickness from photographs that can be obtained with a scanning electron microscope (SEM).

According to a particular embodiment of the present invention, the membrane provided with at least one catalyst layer comprises 0.01 to 20 mg/cm^2, 0.1 to 10.0 mg/cm^2, preferably 0.3 to 6.0 mg/cm^2 and particularly preferably 0.3 to 3.0 mg/cm^2 (sum of all precious metals). These values can be determined by elemental analysis of a flat specimen.

Furthermore, the membrane which can also be provided with a catalyst layer can further be cross-linked by action of heat in the presence of oxygen. This curing of the membrane additionally improves the properties of the membrane. To this end, the membrane can be heated to a temperature of at least 150°C, preferably at least 200°C and particularly preferably at least 250°C. In this process step, the oxygen concentration usually is in the range of from 5 to 50% by volume, preferably 10 to 40% by volume; however, this should not constitute a limitation.

The cross-linking can also take place by action of IR or NIR (IR = infrared, i.e. light having a wavelength of more than 700 nm; NIR = near-IR, i.e. light having a wavelength in the range of from about 700 to 2000 nm and an energy in the range of from about 0.6 to 1.75 eV, respectively). Another method is ß-ray irradiation. In this connection, the irradiation dose is from 5 and 200 kGy.

Depending on the degree of cross-linking desired, the duration of the cross-linking reaction can be within a wide range. Generally, this reaction time is in the range of

from 1 second to 10 hours, preferably 1 minute to 1 hour; however, this should not constitute a limitation.

A membrane electrode unit according to the invention exhibits a surprisingly high power density. According to a particular embodiment, preferred membrane electrode units accomplish a current density of at least 0.3 A/cm^2, preferably 0.4 A/cm^2, particularly preferably 0.5 A/cm^2. This current density is measured in operation with pure hydrogen at the anode and air (approx. 20% by volume of oxygen, approx. 80% by volume of nitrogen) at the cathode, with standard pressure (1013 mbar absolute, with an open cell outlet) and a cell voltage of 0.6 V. In this connection, particularly high temperatures in the range of from 150-200°C, preferably 160-180°C, in particular 170°C can be applied.

The power densities mentioned above can also be achieved with a low stoichiometry of the fuel gases on both sides. According to a particular aspect of the present invention, the stoichiometry is less than or equal to 2, preferably less than or equal to 1.5, very particularly preferably less than or equal to 1.2.

According to a particular embodiment of the present invention, the catalyst layer has a low content of precious metals. The content of precious metals of a preferred catalyst layer which is comprised by a membrane according to the invention is preferably not more than 2 mg/cm^2, in particular not more than 1 mg/cm^2, very particularly preferably not more than 0.5 mg/cm^2. According to a particular aspect of the present invention, one side of a membrane exhibits a higher metal content than the opposite side of the membrane. Preference is given to the metal content of the one side being at least twice as high as the metal content of the opposite side.

For further information on membrane electrode units, reference is made to the technical literature, in particular the patents US-A-4,191,618, US-A-4,212,714 and US-A-4,333,805. The disclosure contained in the above-mentioned citations [US-A-4,191,618, US-A-4,212,714 und US-A-4,333,805] with respect to the structure and production of membrane electrode units as well as the electrodes, gas diffusion layers and catalysts to be chosen is also part of the description.

Examples:

Table 1 shows the cell voltages of 4 different membrane electrode units at current densities of 0.2 A/cm^2 and 0.5 A/cm^2, respectively. The values were recorded in a single fuel cell with an active area of 50 cm^2 at 160°C. Pure hydrogen served as the anode gas (with a stoichiometry of 1.2 and a pressure of 1 bar_a), air served as the cathode gas (with a stoichiometry of 2 and a pressure of 1 bar_a). The composition of the individual specimens is described below:

Specimen 1:
Anode A: The anode catalyst is Pt on a carbon support. The electrode loading is 1 mg_{Pt}/cm^2.
Cathode B: The cathode catalyst is Pt on a carbon support. The electrode loading is 1 mg_{Pt}/cm^2.
Membrane A: A polymer membrane doped with phosphoric acid, the polymer of which consists of poly-((2,2'-m-phenylene)-5,5'-bisbenzimidazole)-co-poly-((2,5-pyridine)-5,5'-bisbenzimidazole), serves as the membrane.

Specimen 2:
Anode A: The anode catalyst is Pt on a carbon support. The electrode loading is 1 mg_{Pt}/cm^2.
Cathode B: The cathode catalyst is Pt on a carbon support. The electrode loading is 1 mg_{Pt}/cm^2.
Membrane B: A polymer membrane doped with phosphoric acid, the polymer of which consists of poly-((2,2'-m-phenylene)-5,5'-bisbenzimidazole), serves as the membrane.

Specimen 3:
Anode A: The anode catalyst is Pt on a carbon support. The electrode loading is 1 mg_{Pt}/cm^2.
Cathode B: The cathode catalyst is a PtNi alloy on a carbon support. The electrode loading is 1 mg_{Pt}/cm^2. The ratio of Pt to Ni is 1:1.
Membrane A: A polymer membrane doped with phosphoric acid, the polymer of which consists of poly-((2,2'-m-phenylene)-5,5'-bisbenzimidazole)-co-poly-((2,5-pyridine)-5,5'-bisbenzimidazole), serves as the membrane.

Specimen 4:
Anode A: The anode catalyst is Pt on a carbon support. The electrode loading is 1 mg_{Pt}/cm^2.

Cathode B: The cathode catalyst is a PtNi alloy on a carbon support. The electrode loading is 1 mg_{Pt}/cm^2. The ratio of Pt to Ni is 1:1.
Membrane B: A polymer membrane doped with phosphoric acid, the polymer of which consists of poly-((2,2'-m-phenylene)-5,5'-bisbenzimidazole), serves as the membrane.

By comparing specimen 1 and 2, which include the same electrodes and Pt catalysts but the differing membranes A and B, it can be seen that, by using membrane B, an only very slight increase of the cell voltage by 3 and 4 mV at 0.2 and 0.5 A/cm^2, respectively, can be achieved. If the cathode (specimen 3 with membrane A and specimen 4 with membrane B) is changed to an alloy catalyst, as is described in this specification, the anode with Pt catalyst remaining the same, the cell voltage can be increased substantially. In this way, the cell voltage increases by 22 mV at 0.2 A/cm^2 with membrane A if said alloy catalyst is employed. Using membrane B, the cell voltage increases by 37 mV at 0.2 A/cm^2 if an alloy catalyst is employed.

Table 1:

No.	Cathode catalyst	Membrane	Cell voltage in [V] at 0.2 A/cm^2	0.5 A/cm^2
1	Pt/C, 1 mg_{Pt}/cm^2	A	0.634	0.555
2	Pt/C, 1 mg_{Pt}/cm^2	B	0.637	0.559
3	PtNi/C, 1 mg_{metal}/cm^2	A	0.656	0.571
4	PtNi/C, 1 mg_{metal}/cm^2	B	0.674	0.598

Claims:

1. A membrane electrode unit comprising
   A) at least one polymer membrane which includes at least one polymer with at least one nitrogen atom, the polymer membrane including at least one mineral acid,
   B) at least two electrodes,

   characterized in that at least one electrode includes a catalyst containing
   i. at least one precious metal of the platinum group, in particular Pt, Pd, Ir, Rh, Os, Ru, and/or at least one precious metal Au and/or Ag
   ii. at least one metal less precious according to the electrochemical series as the metal mentioned in (i.), in particular selected from the group of Fe, Co, Ni, Cr, Mn, Zr, Ti, Ga, V.

2. The membrane electrode unit according to claim 1, characterized in that a polyphosphazene is employed as the polymer with at least one nitrogen atom.

3. The membrane electrode unit according to claim 1, characterized in that an alkaline polymer with at least one nitrogen atom in a repeating unit is used as the polymer with at least one nitrogen atom.

4. The membrane electrode unit according to claim 3, characterized in that the alkaline polymer contains at least one aromatic ring with at least one nitrogen atom.

5. The membrane electrode unit according to claim 4, characterized in that the alkaline polymer is a polyimidazole, a polybenzimidazole, a polybenzothiazole, a polybenzoxazole, a polytriazole, a polyoxadiazole, a polythiadiazole, a polypyrazole, a polyquinoxaline, a poly(pyridine), a poly(pyrimidine) or a poly(tetrazapyrene).

6. The membrane electrode unit according to claim 3, characterized in that a mixture of one or more alkaline polymers with another polymer is employed.

7. The membrane electrode unit according to claim 1, characterized in that the membrane comprises phosphoric acid and/or sulphuric acid as the mineral acid, preferably doped in the polymer membrane.

8. The membrane electrode unit according to one or more of claims 1 to 7, characterized in that the polymer membrane comprises para-polybenzimidazoles.

9. The membrane electrode unit according to one or more of claims 1 to 8, characterized in that the polymer membrane can be obtained by a process comprising the steps of
   i) preparation of a mixture comprising
      polyphosphoric acid,
      at least one polyazole and/or at least one or more compounds which are suitable for the formation of polyazoles with action of heat in accordance with step ii),
   ii) heating the mixture obtainable in accordance with step i) under inert gas to temperatures of up to 400°C,
   iii) applying a layer using the mixture in accordance with step i) and/or ii) to a support,
   iv) treatment of the membrane formed in step iii).

10. The membrane electrode unit according to claim 9, characterized in that the mixture produced in step i) comprises one or more aromatic and/or heteroaromatic tetraamino compounds and one or more aromatic and/or heteroaromatic carboxylic acids or their derivatives, which comprise at least two acid groups per carboxylic acid monomer, and/or one or more aromatic and/or heteroaromatic diaminocarboxylic acids which are suitable for the formation of polyazoles with action of heat in accordance with step ii).

11. The membrane electrode unit according to claim 9, characterized in that the mixture produced in step i) comprises compounds which are obtainable by reaction of one or more aromatic and/or heteroaromatic tetraamino compounds with one or more aromatic and/or heteroaromatic carboxylic acids or their derivatives, which contain at least two acid groups per carboxylic acid monomer, or of one or more aromatic and/or heteroaromatic diaminocarboxylic acids in the melt at temperatures of up to 400°C, which are suitable for the formation of polyazoles with action of heat in accordance with step ii).

12. The membrane electrode unit according to claim 10 or 11, characterized in that the compounds suitable for the formation of polyazoles as aromatic and/or heteroaromatic tetraamino compound comprise compounds which are selected

from the group consisting of 3,3',4,4'-tetraaminobiphenyl, 2,3,5,6-tetraaminopyridine and/or 1,2,4,5-tetraaminobenzene.

13. The membrane electrode unit according to claim 10, 11 or 12, characterized in that the compounds suitable for the formation of polyazoles as aromatic and/or heteroaromatic carboxylic acids or their derivatives, which contain at least two acid groups per carboxylic acid monomer, comprise compounds which are selected from the group consisting of isophthalic acid, terephthalic acid, phthalic acid, 5-hydroxyisophthalic acid, 4-hydroxyisophthalic acid, 2-hydroxyterephthalic acid, 5-aminoisophthalic acid, 5-N,N-dimethylaminoisophthalic acid, 5-N,N-diethylaminoisophthalic acid, 2,5-dihydroxyterephthalic acid, 2,5-dihydroxyisophthalic acid, 2,3-dihydroxyisophthalic acid, 2,3-dihydroxyphthalic acid, 2,4-dihydroxyphthalic acid, 3,4-dihydroxyphthalic acid, 3-fluorophthalic acid, 5-fluoroisophthalic acid, 2-fluoroterephthalic acid, tetrafluorophthalic acid, tetrafluoroisophthalic acid, tetrafluoroterephthalic acid,1,4-naphthalenedicarboxylic acid, 1,5-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid, diphenic acid, 1,8-dihydroxynaphthalene-3,6-dicarboxylic acid, diphenyl ether-4,4'-dicarboxylic acid, benzophenone-4,4'-dicarboxylic acid, diphenylsulphone-4,4'-dicarboxylic acid, biphenyl-4,4'-dicarboxylic acid, 4-trifluoromethylphthalic acid, 2,2-bis-(4-carboxyphenyl)hexafluoropropane, 4,4'-stilbenedicarboxylic acid, 4-carboxycinnamic acid or their C1-C20 alkyl esters or C5-C12 aryl esters or their acid anhydrides or their acid chlorides.

14. The membrane electrode unit according to claim 10, 11, 12 or 13, characterized in that the compounds suitable for the formation of polyazoles comprise aromatic tricarboxylic acids, their C1-C20 alkyl esters or C5-C12 aryl esters or their acid anhydrides or their acid halides, or tetracarboxylic acids, their C1-C20 alkyl esters or C5-C12 aryl esters or their acid anhydrides or their acid halides.

15. The membrane electrode unit according to claim 14, characterized in that the aromatic tricarboxylic acids comprise compounds which are selected from the group consisting of 1,3,5-benzenetricarboxylic acid (trimesic acid); 2,4,5-benzenetricarboxylic acid (trimellitic acid); (2-carboxyphenyl)iminodiacetic acid, 3,5,3'-biphenyltricarboxylic acid; 3,5,4'-biphenyltricarboxylic acid; 2,4,6-pyridinetricarboxylic acid, benzene-1,2,4,5-tetracarboxylic acids; naphthalene-1,4,5,8-tetracarboxylic acids, 3,5,3',5'-biphenyltetracarboxylic

acids, benzophenonetetracarboxylic acid, 3,3',4,4'-biphenyltetracarboxylic acid, 2,2',3,3'-biphenyltetracarboxylic acid, 1,2,5,6-naphthalenetetracarboxylic acid and/or 1,4,5,8-naphthalenetetracarboxylic acid.

16. The membrane electrode unit according to claim 14 or 15, characterized in that the content of tricarboxylic acid and/or tetracarboxylic acids is between 0 and 300 mol-%, preferably 0.1 and 20 mol-%, in particular 0.5 and 10 mol-%, based on dicarboxylic acid used.

17. The membrane electrode unit according to one or more of claims 10 to 16, characterized in that the compounds suitable for the formation of polyazoles comprise heteroaromatic dicarboxylic acids, tricarboxylic acids and/or tetracarboxylic acids, which contain at least one nitrogen, oxygen, sulphur or phosphorus atom in the aromatic group.

18. The membrane electrode unit according to claim 17, characterized in that pyridine-2,5-dicarboxylic acid, pyridine-3,5-dicarboxylic acid, pyridine-2,6-dicarboxylic acid, pyridine-2,4-dicarboxylic acid, 4-phenyl-2,5-pyridinedicarboxylic acid, 3,5-pyrazoledicarboxylic acid, 2,6-pyrimidinedicarboxylic acid, 2,5-pyrazinedicarboxylic acid, 2,4,6-pyridinetricarboxylic acid, benzimidazole-5,6-dicarboxylic acid and their C1-C20 alkyl esters or C5-C12 aryl esters or their acid anhydrides or their acid chlorides are employed.

19. The membrane electrode unit according to claim 10 or 11, characterized in that the compounds suitable for the formation of polyazoles comprise diaminobenzoic acid and/or its monohydrochloride and dihydrochloride derivatives.

20. The membrane electrode unit according to any one of claims 10 to 19, characterized in that at least one para-dicarboxylic acid is employed.

21. The membrane electrode unit according to one or more of claims 10 to 20, characterized in that the heating in accordance with step ii) is performed after the formation of a flat structure in accordance with step iii).

22. The membrane electrode unit according to any one of claims 10 to 21, characterized in that the membrane formed according to step iv) has a thickness between 15 and 3000 µm.

23. The membrane electrode unit according to any one of claims 1 to 22, characterized in that the catalyst contains
    i. at least one precious metal of the platinum group, in particular Pt, Pd, Ir, Rh, Os, Ru, and/or at least one precious metal Au and/or Ag
    ii. at least one metal less precious according to the electrochemical series as the metal mentioned in (i.), in particular selected from the group of Fe, Co, Ni, Cr, Mn, Zr, Ti, Ga, V.

24. The membrane electrode unit according to any one of claims 1 to 23, characterized in that the catalyst is applied to the polymer membrane.

25. The membrane electrode unit according to one or more of claims 1 to 24, characterized in that the catalyst layer has a thickness in the range of from 0.1 to 50 µm.

26. The membrane electrode unit according to one or more of claims 1 to 25, characterized in that the catalyst comprises catalytically active particles which have a size in the range of from 5 to 200 nm.

27. The membrane electrode unit according to one or more of claims 1 to 26, characterized in that the catalyst comprises catalytically active particles on a support, the size of the catalyst particles being in the range of from 1 to 20 nm.

28. The membrane electrode unit according to one or more of claims 1 to 27, characterized in that the membrane electrode unit comprises 0.01 to 20 g/m^2, preferably 0.1 to 10 g/m^2, of a catalytically active substance.

29. The membrane electrode unit according to claim 27, characterized in that the catalytically active particles include carbon as a support.

30. The membrane electrode unit according to one or more of claims 1 to 29, characterized in that the weight ratio of the precious metals of the platinum group or of Au and/or Ag (i) to the metals less precious according to the electrochemical series (ii) is between 1:100 to 100:1.

31. A fuel cell containing one or more membrane electrode units according to one or more of claims 1 to 30.

Abstract

High-performance membrane electrode unit and the use thereof in fuel cells

The present invention relates to a membrane electrode unit comprising a polymer membrane doped with a mineral acid as well as two electrodes, characterized in that the polymer membrane comprises at least one polymer with at least one nitrogen atom and at least one electrode comprises a catalyst which is formed from at least one precious metal and at least one metal less precious according to the electrochemical series.